

**RECOVERY OF STEEL FROM CONTAMINATED SCRAP**

This invention relates to a method and apparatus for recovering value-added steel from steel scrap contaminated principally with zinc, copper and tin and also possibly other deleterious non-ferrous metal impurities. It also relates to steel contaminated with carbonaceous material either because it stems from organic coated steel substrates either alone or in composite coatings comprised of organic coating in combination with zinc or other non-ferrous metal coating of such steel substrate material or, alternatively, carbonaceous material that is present adventitiously due to contamination with unconsumed foodstuffs or other vegetable matter.

In certain cases the aforementioned examples of contaminated scrap may be treated individually in isolation if sufficient quantities are readily available. More generally, to save labour intensive and thus costly sorting, the intermixed scrap materials constitute the feed for the method of this invention for recovery of high quality steel along with a range of valuable by-products.

According to Japanese workers (K. Shibata et al.: *Materials Transactions*, 2002, vol. 43, No. 3, 292-300) not only is the amount of steel scrap increasing but, in addition the quality of the steel scrap is decreasing, especially because of increased concentrations of copper and tin. Copper is derived from components found in electrical equipment such as wiring of motors and that associated with cars and home electronic equipment. Tin stems mainly from tin plate during manufacture as well as tin plated cans reporting in domestic refuse. Once these elements are incorporated into a steel melt, they are traditionally regarded as being difficult to remove.

Copper creates a serious problem during mechanical working at high temperatures such as hot rolling and forging, which is well documented and is referred to as hot shortness. In effect, copper causes cracks to form on the steel surface during hot working by a mechanism involving enrichment of copper at the steel/scale interface by selective oxidation of iron. The copper enriched phase liquefies and penetrates into austenite grain boundaries under stress during hot rolling or forging to initiate surface cracking. From the viewpoint of recycling of steel, surface hot shortness is generally regarded as the most serious problem. Unfortunately, tin accelerates this deleterious influence of copper and therefore there are strict limitations on the permitted copper and tin contents in each kind of steel.

Obsolete and heavily contaminated steel scrap is steadily increasing worldwide year by year. Scientists and engineers have been aware of this accumulation for decades but despite many attempts to ameliorate the problem, no successful commercial technology has yet been developed, which would permit substantial reduction of this locked-up resource stockpile. It is only the higher quality fraction that is recycled directly into existing steelmaking processes of the present generation. Additional inroads into the vast scrap stockpile of obsolete scrap are made by various chemical and physical treatments away from the steelmaking site to reduce the amounts of so-called tramp elements to a level currently acceptable for steelmaking, but the extent of this is severely limited by economic factors, despite the fact that melting of scrap is by far the lowest energy route to steel. Accordingly, virgin iron ore materials are still being consumed as the major source of iron units worldwide, despite the adverse energy consumption implications and its negative impact on sustainability, climate change and global warming.

A process that can handle galvanized and organic-coated steel along with segregated shredded auto scrap, the magnetic fraction of incinerated urban refuse, segregated tin cans along with higher quality steel scrap, will out

perform the best available technology. It will have access to the most competitively priced iron units available at a given time and will be flexible enough to change its feed as economic conditions dictate.

The inventor has had a long-standing involvement with the fundamental aspects of ironmaking and steelmaking and can rightly claim major contributions in both areas. As long ago as 1964 he successfully challenged a series of papers emanating from the US Steel Corporation Research Laboratory on the kinetics of the gaseous reduction of hematite and in 1966 he was co-recipient in New York of the Robert W. Hunt Award of the AIME. The Hunt Award paper unequivocally demonstrated the central role of gaseous diffusion in the primary steelmaking reaction. Since then he has witnessed countless unsuccessful attempts to introduce continuous steelmaking over the decades, yet has remained convinced that the best way forward for dealing with steel scrap contaminated with non-ferrous metals was to focus on truly continuous steelmaking and the immediate benefits that success in this area would confer on the steel industry.

A key feature of truly continuous processing, which is just not available with present steelmaking technology, is the ability to in-line continuously incorporate impure steel scrap directly within the overall steelmaking circuit without prior treatment, except perhaps simple physical segregation at point of origin. This must secure a valuable competitive advantage. According to Boom and Steffen (R. Boom and R. Steffen: *Steel Research*, 2001, vol. 72 (3), pp. 91-96) recycling for high quality steel products has been the focus recently of a group of steel producers and research institutes in the European Union. In contra-distinction to the approach advocated in their studies, pre-treatment of steel scrap away from the steelplant, other than simple physical segregation at point of origin, is considered by the applicant to be unnecessary and counter-productive. What is needed is technology that in-line treats liquid scrap as it enters the main continuous steelmaking circuit. The chemistry involved should be straightforward and preferably the operations should have predictable performance to ensure that scale-up to full-size commercial plant proceeds smoothly without unanticipated difficulties. Absorption and desorption are the unit operations of prime significance in this regard. These processes are physically reversible and do not rely on complex chemical interfacial kinetics for their effectiveness. However, current technology for steelmaking is essentially batchwise processing and thus incompatible with this approach. Therefore, development of truly continuous steelmaking is a vital pre-requisite, if the benefit of in-line processing and all this entails are to be secured.

According to the present invention, there is provided a method of recovering a high quality steel product from contaminated steel scrap from a high temperature steelmaking circuit from which said steel can be produced continuously, the method comprising the steps of:

1. preheating the solid scrap in a protective gas atmosphere to separate out a molten zinc by-product prior to the scrap being assimilated into a forced-circulated stream of molten scrap (liquid scrap) within a closed-loop melt circulation system, fired on one side with combustion gases derived from natural gas or, alternatively, combustible process gases derived initially from carbothermic reduction of virgin iron ore material;
2. overflowing, withdrawing or siphoning out continuously the liquid scrap and incorporating it into a gas-lift pumping device which feeds the liquid scrap to the top of the first of two reduced pressure packed towers or similar devices, in which the liquid scrap is raised in temperature from near its liquidus temperature to a very much higher temperature, possibly approaching the technical upper limit of available commercial refractories, by electrical

conductive heating, before allowing it to irrigate the solid packing and flow downwards by gravity as rivulets or discrete droplets against an upward flow of strip gas at reduced pressure, which volatilizes elemental copper impurity dissolved in the liquid scrap, but only a relatively smaller amount of dissolved elemental tin, whilst itself becoming almost saturated with iron vapour;

3. withdrawing continuously via a barometric leg the now de-copperized liquid scrap into an atmospheric pressure sump and then into a second gas-lift pumping system employing a lift-gas to which elemental sulphur or gaseous sulphur or sulphur compound gas has been added to the extent that the liquid scrap absorbs sulphur so that greater than the stoichiometric requirement for all the dissolved tin to potentially form stannous sulphide is provided;
4. admitting the liquid scrap into the top of a second reduced pressure packed tower or similar device and using electrical conductive or radiative heating to increase the liquid scrap temperature up towards the service limit of suitable commercially available refractories prior to contacting the liquid scrap with an inert strip gas so that stannous sulphide is volatilized from the liquid scrap as it flows by gravity through the tower;
5. withdrawing continuously via a barometric leg the now de-tinned and de-copperized liquid scrap into an atmospheric pressure sump, from which the non-ferrous metal depleted liquid scrap is overflowed or siphoned continuously into an open-channel melt circulation loop in which low carbon steel is forced circulated at a rate many times that of the flow of the liquid scrap added to it, whilst the melt is desulphurized by addition of an appropriate flux or other established desulphurization means, and the carbon and oxygen contents adjusted to the required level, typically by carbon addition or  $\text{CO}_2/\text{H}_2\text{O}$  gaseous oxidation;
6. overflowing or siphoning out continuously refined low carbon steel to a continuous casting facility or, alternatively, interposing an additional in-line ultra-low carbon (ULC) refining step in advance of its transmission to a continuous casting facility.

If a high scrap contaminated feed is to be processed, valuable by-product credits must be sought, if at all possible, to at least partly offset the additional processing costs introduced. For the approach proposed in this invention, the tin impurity is regenerated to metallic tin within the process. The zinc is principally converted to a liquid zinc by-product and the balance to a low-iron zinc sulphide concentrate, ideal to supplement natural zinc concentrates for a Primary Zinc producer. The copper impurity is recovered in metallic form, which will yield on fire refining a high quality ingot copper as a by-product.

New reactor concepts for continuous coal-based integrated ironmaking and steelmaking have been identified (N.A. Warner: *Proc. Yazawa Int. Symp. On Metallurgical and Materials Processing*, 132<sup>nd</sup> TMS Annual Meeting, San Diego, CA, March 2-6, 2003, vol. 1, pp. 881-900, TMS Warrendale, Pa.), which would appear to be ideally suited to the present requirements. It has been proposed that iron ore fines, granular coal/pulverized coal and lime flux be dried and intimately mixed together before charging onto the top surface of the moving Fe-C melt on the charge side of the ironmaking loop, the first of three melt circulation loops. The other two loops continuously refine the solid metallized material produced in the ironmaking loop down to molten low carbon steel with in-line desulphurization and dephosphorization using *in situ* generated fluxes. The charge progresses in a straight line, initially as a sheet of

composite material floating on the circulating Fe-C of the first loop, and is transported along as it is transformed in the first instance into a sintered raft of partially reacted solid material with the thermal and chemical reaction fronts progressing upwards from the charge/liquid metal interface.

The first of the two steelmaking loops is top-blown on both arms, whilst the second is merely two open channels. Both are carefully designed so that the supply of oxidant to the liquid metal surface balances the liquid phase mass transfer of carbon from the bulk to the interface. By so doing, sub-surface nucleation and growth of CO bubbles are precluded, making it possible to sustain zero ejection of micro-spray and fume formation right down from say a nominal 4 percent Fe-C melt to 0.03 percent carbon in the open channel loop. Further details concerning the proposed continuous steelmaking process are given in PCT/GB2003/003065 and PCT/GB2003/003069.

Liquid steel scrap may be introduced into the melt circulation circuit of the above at two distinctly different locations. If tin is to be removed, then sulphur containing gas initially derived from the ironmaking loop is contacted with the tin containing melt to enable continuous vacuum desorption of volatile stannous sulphide before the liquid scrap enters the primary steelmaking loop so that in-line desulphurization can be effected in concert with the virgin iron produced in the ironmaking loop.

If tin contamination is not an issue, then in-line removal of zinc by simple desorption at atmospheric pressure and physical desorption of copper under reduced pressure is effected before the liquid scrap joins the melt in the open-channel decarburization loop so that the desired final carbon content of the metal can be attained in this loop and then, if so required, the continuous overflow from the open-channel loop can become the feed stream to a liquid-metal irrigated packed bed, the ultra low carbon (ULC) Tower Refiner. Alternatively, it can feed directly to continuous casting.

In this invention steel scrap is melted and then introduced into an overall steelmaking circuit by a further adaptation of melt circulation technology. This time a melting loop, similar to the main steelmaking loops described above, has preheated scrap melting on one arm and on the other radiant heat input either by natural gas combustion with air, if a zero gas emission scenario is not being pursued or alternatively, if zero gas emission is the ultimate objective and integrated ironmaking and steelmaking the preferred way forward, then the scrap melting loop utilizes the oxidizing gases exiting the post combustion arm of the ironmaking loop. By design, convective mass transfer is restricted to ensure liquid scrap oxidation is insignificant on the heat transfer arm, while maintenance of an argon or other protective atmosphere on the melting arm avoids yield losses by oxidation. The protective atmosphere extends from the molten bath right back through charge preheating, initially by radiation and then at the feed end by convection. Scrap addition to the convective preheater is via initial submergence in a water seal so that air ingress is precluded. This means that the recirculating protective atmosphere has to be de-watered and dried, probably using pressure swing adsorption as, for example, patented for maintaining the protective atmosphere in float glass technology.

Another closed loop melt circulation loop employing molten aluminum as a heat transfer medium with electromagnetic melt circulation as used extensively in the secondary aluminum industry, coupled with the well-established mechanical rotor/splash system developed for the zinc blast furnace, will provide the high intensity liquid-metal based convective heat transfer to the recirculating argon to sustain scrap preheating and melting under

benign conditions. On the radiative heat input side, a thin floating layer of calcium chloride flux, for example, prevents the hot combustion gases from oxidizing the molten aluminum, while considerably enhancing radiative heat transfer. The emissivity of liquid aluminum at its melting point is about 0.03 whereas that of fused halide is typically around 0.7 to 0.75.

It is considered that the proposal just outlined is a solution to the drawbacks of scrap preheating (J.A.T. Jones: *Iron and Steelmaker*, February 1997, pp. 41-42) while capturing the specific objectives listed by the same author in his review of new steel melting technologies. The recirculating argon scheme is not, of course, entirely zero gas emission because a small bleed will always be necessary to release accumulated gaseous contaminants, but these would be subjected to rigorous cleanup before being finally discharged to the atmosphere. In the longer term, post combustion (PC) gases would undergo water condensation before CO<sub>2</sub> sequestration after first being routed to a conventional heat recovery steam generator (HRSG) of the type normally associated with combined cycle power generation.

Liquid metal irrigation of a packed bed for the ultimate refining step is a preferred way forward for removing non-ferrous metal contaminants from liquid scrap, because it has many attributes to commend it. There is no slag and the dissolved gas content is relatively small, so a fixed bed rather than a moving bed is a realistic option. Also because of its inherent simplicity this could be exchanged periodically with a replacement unit as demanded by accretion build up or other adverse operating factors. Accordingly, the overflow from the scrap-melting loop feeds directly by gravity, is transmitted by a hot metal siphon or is gas-lift pumped to a packed bed contactor, in which the continuous stream of liquid scrap is contacted with argon or other appropriate inert gas at reduced pressure. The non-ferrous metal dissolved in the melt diffuses to the large gas-liquid interfacial area characteristic of non-wetting liquid metal irrigation of a packed bed and is then desorbed into the gas phase.

The gas phase is maintained as a continuum and high intensity heat and mass transfer are achieved by allowing the liquid-metal stream to disintegrate and flow downwards as droplets or rivulets by gravity countercurrent to an upward flow of gas within a bed of solid packing material. This of course is what happens in the lower regions of a blast furnace. Formation of accretions within the bed normally has little effect on the operability of the blast-furnace process, because the bed material is ultimately melted or consumed while being continuously replenished from above. In the present case, potential accretion formation dictates either a readily replaceable fixed bed or alternatively a moving bed configuration with solid packing elements being cleaned externally. Because the downward movement is relatively slow in comparison with the velocities of the upward flowing gas and the droplets or rivulets of liquid metal irrigating the solid packing, quantitative treatment for the latter can be based also on fixed-bed behaviour.

The vitally important difference between liquid-metal irrigation of a packed bed and that normally encountered in the chemical industry and elsewhere is the fact that liquid metals normally do not wet solid packings. In the laboratory this non-wetting flow can be simulated by treating the solid with paraffin wax and then conducting normal gas absorption, humidification or de-humidification with water irrigation. By these means it is possible to elucidate the mechanisms of the associated high-temperature mass and heat transfer phenomena by analogy using relevant dimensionless groups or empirical relationships. In 1953 the applicant was the first to adopt this approach in a high

temperature metallurgical context in order to demonstrate that the so-called condenser of a zinc-lead blast furnace is not in fact a condenser but rather a gas absorber, which operates under exclusive gas diffusion control (N.A. Warner: *Mineral Processing and Extractive Metallurgy (Trans. Inst. Min. Metall. C)*, 2003, vol. 112, no. 3, pp. C141-C154). This gave developers of the process the theoretical platform from which to effect considerable improvement in condensation efficiency of zinc and therefore profitability for its licensees.

Flooding in non-wetting systems has been investigated by several workers because of its importance to the iron blast furnace. The present most relevant experimental data are for flooding velocities in mercury irrigation of packed beds (J. Szekeley and J. Mendrykowski: *Chemical Engineering Science*, 27, 1972, 959-963). The approach used by them was based on the standard representation of flooding phenomena originally put forward for normal wetting systems. Flooding velocities for water irrigation of waxed solid packings have also been reported (N. Standish: *Chem. Eng. Sci.*, 1973, Vol. 28, 1906). In general, non-wetting systems do not flood as readily as wetted systems and liquid metals can sustain much higher rates than predicted by the wetting correlation. This in turn translates into smaller pressure vessels than would otherwise have been the case for similar gas and liquid throughputs.

A new assessment of experimental non-wetting mass transfer data in water irrigated packed beds in combination with data on mercury vaporization in packed beds has been published (N.A. Warner: *Ironmaking & Steelmaking*, 2003, vol. 30 (6), 435-440) and empirical correlations developed for the heights of gas phase and liquid phase transfer units in non-wetting irrigated packed bed systems. The transfer unit concept assists comprehension of the physical significance of mass and heat transfer calculations by breaking the fundamental processes down to two terms. The first for gas-phase transfer is a measure of the difficulty of the operation, expressed by the dimensionless number of transfer units ( $N_G$ ) and the second is the height of a transfer unit ( $H_G$ ) with length dimensions. The required linear dimension of the contactor, either length or height, is simply the product of  $N_G$  and  $H_G$ . The analogous terms for liquid phase mass transfer are  $N_L$  and  $H_L$ , respectively.

In mathematical terms, the mass transfer correlations are given in Equation 1 for liquid-phase mass transfer and Equation 2 for gas-phase mass transfer. In these equations the fluid properties are expressed in terms of viscosity  $\mu$  and density  $\rho$ . The flow rates used are the mass velocity of the liquid  $L$  and the true gas velocity  $v_g$ . The correlations apply to non-wetting conditions of the type likely to be encountered in advanced continuous steelmaking, but should in principle only be used within the experimentally verified range of the dimensionless groups. However, in the present case, this was not always possible, so extrapolation was unavoidable. It should also be borne in mind that the correlations are not dimensionless but are expressed in SI units. If the missing length dimensions in the abscissas are incorporated, then the correlating modulus is seen to be the dimensionless Reynolds Number. The dimensionless Schmidt Number ( $Sc$ ) and the exponents of  $-1/2$  and  $-2/3$  reflect usage in other well-established mass transfer correlations for liquid-phase and gas-phase mass transfer, respectively. The characteristic dimension  $d_s$ , defined as the diameter of a sphere having the same surface area as the packing element in the gas-phase correlations, covers a range of packing elements including 1/4 inch and 1/2 inch Raschig rings and 10 mm, 20 mm and 45 mm diameter spheres. For liquid-phase mass transfer 20 mm, 45 mm and 150 mm spheres were used. The effect of flowrate of the irrigating liquid under non-wetting conditions is accounted for by the volumetric flux  $L_o$  expressed as

$\text{m}^3/(\text{s})(\text{m}^2)$  and empirically the exponent is determined as -0.23. The heights of transfer units  $H_L$  and  $H_G$  are in metres.

$$\left(\frac{H_L}{d_s}\right) = 0.0571 \left(\frac{L}{\mu}\right)^{0.290} \text{Sc}^{1/2} \quad [1]$$

$$\left(\frac{H_G}{d_s}\right) = 0.0684 \left(\frac{v_g \rho}{\mu}\right)^{0.376} \text{Sc}^{2/3} \text{Lo}^{-0.23} \quad [2]$$

The above correlations have been used previously (N.A. Warner: *Ironmaking & Steelmaking*, 2003, vol. 30 (6), 435-440) to evaluate transformation of low carbon steel to ultra low carbon (ULC) steel using a Tower Refiner in continuous steelmaking. The additive diffusional resistance concepts previously used by the applicant for the ULC case have now been applied to desorption of zinc, copper and tin from liquid scrap. The results of this theoretical analysis are summarized below:-

1. Zinc not removed from galvanized scrap during preheating in argon and “sweated out” immediately as a liquid zinc by-product, can be removed from liquid scrap in two stages. Firstly, within the scrap melting loop on the charge arm downstream from the zone in which preheated solid scrap is being assimilated, profiling the roof so that the freeboard is reduced to about 0.1m allows a controlled addition of purge gas to readily desorb zinc from the melt surface such that the steady-state concentration of zinc throughout the melting loop is in the region of 500ppm. This means that for a raw scrap feed containing 1% zinc initially, some 95% of the zinc is either “sweated out” or desorbed at atmospheric pressure into a purge gas as zinc vapour. The overflow from the melting loop is removed continuously, perhaps by a hot metal siphon into a countercurrent contactor. One option for this is an irrigated packed tower in which a small amount of purge gas is used to strip the zinc from say 500ppm to 5ppm, again at atmospheric pressure. The de-zincd liquid scrap then flows directly into the main continuous steelmaking circuit. It can be shown that more than 85% of the diffusional resistance in this case is in the liquid phase. This is an interesting result in that it contrasts sharply with the applicant’s previous analysis of the fundamental mechanism involved in the so-called condenser of a zinc blast furnace (N.A. Warner: *Chem. Eng. Sci.*, 1959, Vol. 11, 161-182), an example of almost exclusive gas-phase mass transfer control.

2. For desorption of copper and tin, it can be established that atmospheric pressure operation is not feasible. However, for desorption under reduced pressure into a strip gas there is no fundamental problem with high-level removal of copper by such treatment, but with tin it is necessary to desorb volatile stannous sulphide. Therefore, tin removal is no longer the simple reversible process of physical desorption, but rather chemical reaction at the gas/melt interface must take place before  $\text{SnS}_{(g)}$  is desorbed into the strip gas. Accordingly, one must proceed with caution in the tin contaminated scrap case. However, if it is assumed that the chemical reaction proceeds very rapidly at the proposed temperature level of 1780°C, then thermodynamic equilibrium is established at the interface. The additive diffusional resistance principles are then valid and the key parameters for the plant can then be defined.

Hino et al.(M. Hino, S. Wang, T. Nagasaka and S.Ban-ya: *ISIJ International*, 1994, vol. 4, pp. 491-497) studied the evaporation of zinc from liquid iron using a top-blown argon jet at atmospheric pressure onto an inductively stirred

melt and concluded that under their conditions liquid-phase mass transfer was rate controlling once the top blow rate exceeded a relatively low value. Their results support the conclusions theoretically established using the correlations given in Equations 1 and 2 for countercurrent contacting employing a purge gas and liquid metal irrigation of a packed bed.

The vaporization of zinc from scrap during preheating in nitrogen and carbon monoxide was reported (B. Ozturk and R.J. Fruehan: *Steelmaking Conference Proc.*, 1996, pp.583-588, The Iron and Steel Society, Warrendale, Pa.) to be very rapid after a temperature of 850°C is reached. Therefore, in an argon recirculating preheat system, as currently under discussion, liquid zinc will reflux in the preheater immediately above the liquid scrap bath and at steady state will drain into the bath at the same rate as zinc not already "sweated off" enters the region in the scrap preheater, beyond where sweated liquid zinc is removed as a by-product.

In view of both the above studies along with the further in-depth consideration given in by the applicant, removal of zinc from scrap based on physical desorption should be a straightforward procedure at the continuous steelmaking plant with most of the zinc being recovered immediately in liquid metallic form. The smaller amount carried off in the purge gas is ideally suited for hot gas clean-up service using zinc based desulphurization and the resulting zinc sulphide recovered should be low in iron and be a premium feedstock for a Primary Zinc producer.

Studies on copper distillation from molten steel have been summarized (R. Harris and W. Davenport: *Cand. Met. Quart.*, 1979, vol. 18, pp. 303-311) and subsequently details of a specific vessel to remove copper and tin from liquid steel, in which a large surface area of steel was exposed to vacuum, were reported (R. Harris: 1983 US Patent 4,378,242). This clearly was a move in the right direction. However, more recently other authors (T. Emi and O. Wijk: *Steelmaking Conference Proc.*, 1996, pp.551-565, The Iron and Steel Society, Warrendale, Pa.; as well as L. Savov, S. Tu and D. Janke: *ISIJ International*, 2000, vol. 40 (7), pp. 654-663) have independently concluded that, at present, removal of copper under vacuum is not practicable as a means for treating scrap on a commercial scale. Notwithstanding this, the real issue to be addressed at temperatures approaching the limits imposed by refractories has been correctly identified (T. Nagasaka, M. Hino and S. Ban-ya: *Steelmaking Conference Proc.*, 1996, pp. 589-596, The Iron and Steel Society, Warrendale, Pa.) as being the difficulty in removing Cu, Sb and Sn to low levels by vacuum treatment, because of the preferential evaporation of iron itself. These authors along with many previous workers advocate separation of tin from iron, based on the vapour pressure of  $\text{SnS}_{(g)}$  rather than attempting to volatilize elemental Sn.

Returning to the problem of iron vaporization, clearly this cannot be prevented, so what is needed is a practical means for condensing liquid iron and returning it to the liquid scrap, while allowing desorbed copper to be recovered, subsequent to iron condensation. In a continuous scrap melting process, this really is not as daunting as it may first appear. The strip gas, effectively saturated with iron vapour, has to be countercurrently contacted with the flow of liquid scrap as it progresses from the scrap-melting loop to the main steelmaking circuit. Fortunately, the total enthalpy of the strip gas containing the iron vapour (sensible heat plus latent heat) is high enough to permit adaptation of the residual unmelted solid shell theme, already exploited for containment of the melt pools or



“swimming pool” reactors, which constitute the various molten iron melt circulation loops, characterizing this new steelmaking process. Generation of high pressure steam by radiation from the outer surfaces of the retained solid shell which surrounds an irrigated packed bed and its associated gas-lift melt circulation system employing liquid scrap close to the liquidus temperature when in operation or when in stand-by or start-up modes conductive heating, is considered to be a viable option. An account of the development of conductive heating and melt circulation in pyrometallurgy has been published recently (N.A. Warner: *Mineral Processing and Extractive Metallurgy (Trans. Inst. Min. Metall. C)*, 2003, vol. 112, no. 3, pp. C141-C154). The semi-pilot scale experiments described therein in general very much influenced the thinking behind the current invention and in particular what now follows.

Consider an assembly of concast slabs stacked on top of each other so that a U configuration is formed with say the vertical arms 7m in diameter and about 1.1m high. The hold-up of steel in this assembly would be less than 1% of the total annual output of a steel plant producing one million tpa. If steps were taken during stacking to ensure good electrical contact, particularly over the outer skin of the assembly extending about 80 mm inwards and a computer designed array of steam boiler tubes were positioned to extract heat from the outer surfaces by radiation, then by passing a heavy AC current through what in effect is a cylinder bent to a U shape and having a total length of about 30 m, it should be possible to generate a stable residual solid shell profile enclosing on one side a liquid steel pool say 5m in diameter (residual solid shell 1m thick) and a cylinder of liquid steel on the other side say 1m in diameter (residual solid shell 3m thick). Furthermore, by careful design it should be possible to establish a conduit of liquid steel connecting together the two columns of liquid steel inside both arms of the original U towards the bottom. If an inert gas is then injected into the base of the 1m diameter column of liquid steel, perhaps by a refractory lance from the top after a hot metal siphon has been positioned so that it interconnects both arms, then a melt circulation loop is created and on increasing the amount of gas injected into the upleg and removing melt from the 5m diameter well, a basket of refractory packing can be so positioned that the melt circulation irrigates the solid packing with a protective gas atmosphere as the continuous phase. Within the basket of removable refractory packing is a centrally located ceramic duct extending downwards and providing support for the packing elements as well as a means for distributing a gas into the base of the packed bed.

In operation, the above arrangement becomes a direct contact iron vapour condenser. When the electric current supply is reduced or switched off altogether and iron vapour condensation commenced, steady state steam generation will be established and the shells of the retained solid should last indefinitely, provided the melt temperature is maintained at the liquidus temperature and the placing of the boiler tubes was correct in the first place, taking into account the various heat flow terms in the heat balance. This, of course, is only an option for a truly continuous steelmaking process.

If difficulties do arise or if the plant is to be put on stand-by or eventually shut down, it will be essential to withdraw all the ancillaries vertically upwards before the whole assembly freezes. However, once fully commissioned it is anticipated that the plant should be relatively straightforward to re-start either from cold or from stand-by mode in which no solidification has yet taken place.

According to Savov et al. (L. Savov, S. Tu and D. Janke: *ISIJ International*, 2000, vol. 40 (7), pp. 654-663), tin plate represents a very low carbon content steel sheet coated with an average of 5g Sn/m<sup>2</sup> and tin plate scrap contains an average 0.2 to 0.4% Sn. Opinion within Europe is probably reflected by the permissible maximum tin content reported by these authors of 0.01% Sn for flat products. For combinations of tin plus copper in steel products, a tolerance level for flat products of  $\text{Cu} + 8 \text{ Sn} < 0.4\%$  has been reported (T. Emi and O. Wijk: *Steelmaking Conference Proc.*, 1996, pp.551-565, The Iron and Steel Society, Warrendale, Pa). These are the guidelines used in formulating the present requirements, but in expectation that these limits are going to be considerably tightened, the prudent approach was to design the new process technology so that it could accommodate these limits in theory by a considerable margin, particularly once dilution in other feed streams contributing to overall steel production are taken into account.

Reference has already been made to the fact that, as opposed to zinc and copper desorption into an inert strip gas under reduced pressure, the elimination of tin as stannous sulphide could be complicated by interfacial chemical kinetics, so caution was advocated in applying the framework of diffusional resistance for interphase mass transfer.

Despite what has been said above, there strong experimental grounds for expecting tin elimination to be transport controlled at the temperature levels now concerned under similar operating conditions. The work of Lui and Jeffes (X. Liu and J.H.E. Jeffes: *Ironmaking & Steelmaking*, 1988, vol. 15 (1), pp. 21-32) gives grounds for cautious optimism in this regard. These authors bubbled argon through molten iron containing various amounts of carbon and tin at atmospheric pressure. Although desorption at 1 atm for a practical industrial process has already been ruled out, the tin elimination rates expected for liquid metal packed-bed contacting under reduced pressure, yields results comparable to those reported by Lui and Jeffes at 1600°C, but because the present evaluation is at a higher temperature level (1780°C inlet temperature), it is to be expected that the actual rates calculated are considerably greater than those observed in the Lui and Jeffes experiments, but so presumably are the intrinsic chemical reaction kinetics. Accordingly, without too much apprehension, it seems reasonable to continue the present evaluation based on transport control, not only for zinc and copper, but also for tin elimination as well.

Lui and Jeffes conclude that the conditions under which de-tinning takes place do not appear to be immediately promising as the basis of a ladle treatment for tin removal, because of the large amount of purge gas required and the sulphur necessary to effect de-tinning in low-carbon alloys. However, the information they generated has been extremely valuable background. With truly continuous steelmaking, the problems identified by these authors are immediately overcome, if desorption of stannous sulphide is carried out under a reduced pressure into an inert strip gas.

Within the above thermodynamic constraints, the process engineering of de-tinning high tin feedstocks is fundamentally the same as that involved in desorption of copper, once it is accepted that sulphur has to be added to the liquid scrap to generate the requisite vapour pressure of stannous sulphide and therefore desulphurization must follow. The comments made (L. Savov, S. Tu and D. Janke: *ISIJ International*, 2000, vol. 40 (7), pp. 654-663) are germane to this situation. They indicate that the application on a larger scale of de-tinning based on SnS evaporation is technically feasible, but, at present, it is hindered by the economics of tinplate scrap recycling and that of

desulphurization. Accordingly, for natural gas firing of the scrap melting loop an in-line desulphurization step has to be introduced into the flowsheet. Alternatively, it may be more rewarding to focus on low tin scrap for the natural gas option, leaving higher tin materials for treatment elsewhere using the integrated ironmaking and steelmaking option proposed by the applicant for this purpose.

With the proposed integrated iron and steelmaking circuit, however, desulphurization is facilitated by continuous processing of liquid scrap in conjunction with the flow of the primary metal from the outset in the first of the steelmaking loops. Clearly, this processing option is not available with current steelmaking technology.

Desulphurization, however, is not needed when processing very low tin scrap. This is a special case in that tin contamination is assessed to be at an acceptable level after dilution with the total iron units charged (virgin plus scrap). Clearly, the total amount of tin charge has to be restricted but the advantage of this approach is twofold. Firstly, stannous sulphide does not have to be vaporized so the precision of the process engineering design is not corrupted by possible interfacial kinetics exerting an influence on the otherwise straightforward and entirely predictable process of physical desorption involved in both zinc and copper elimination. Secondly, sulphur does not have to be added to the liquid scrap, so possibly it can be merely combined with the continuous output of the virgin steelmaking circuit before the combined output goes to continuous casting. Alternatively, the addition of the liquid scrap to the main steelmaking circuit can be delayed to the ULC tower refiner, without increasing the mass flow through decarburization, desulphurization and dephosphorization.

A paper published in 1996 claimed that the traditional electric arc furnace (EAF) steelmaking process had been optimised over the years to such an extent that further improvements in melting capability could be achieved only with considerable complexity and capital expenditure (W. Hofmann, W. Reichelt and R. Fuchs, *Proc. Int. Symp. On Challenges in Process Intensification*, Montreal, Quebec, Aug. 24-29, 1996, Canadian Institute of Mining, Metallurgy and Petroleum, Montreal, Quebec, pp. 291-301). The authors went on to outline the concept of the CONTIARC Continuous Melting Furnace. They pointed out that the electric power demand profile for a modern Ultra High Power (UHP) EAF indicates that the installed power is used on average only 60-70% of the operating time. The rest of the time is taken up by charging, tapping, refractory repairs and periods at which the furnace is run at less than full power, such as running-up after charging, superheating phase, etc. Accordingly, they assert that the melting rate could be increased by a factor of 1.6 of its present level merely by exploiting the margin, if the process was continuously operating, but admit that this would demand a totally new melting method compared with the conventional UHP EAF, and a modified furnace vessel.

Continuous process proponents would have no difficulty in agreeing with all these claims and would also probably acknowledge that, if the electrical energy for melting is provided by nuclear or hydro means, then direct use of fossil fuel (oil, coal or natural gas) is unlikely to compete in energy terms with CONTIARC. However, a totally different picture emerges, if the primary electrical energy is generated with fossil fuel.

In the UK and throughout the world, the majority of electricity is generated by fossil-fired steam boilers in association with steam turbines, typically with steam conditions of 160 bar/568°C/568°C and with overall plant efficiency of 40%. Current state-of-the-art plant has steam conditions 300 bar/600°C/600°C/600°C with an overall

efficiency of 47.5%. The European Union through its Thermie 700°C Project has a target net efficiency within the range 53-55% for advanced pulverized coal-fired plant, but this is going to require massive development of the necessary materials technologies, based principally on the replacement of iron-based alloys by nickel-based alloys to attain the stated-objective steam conditions of 375 bar/700°C/720°C/720°C by 2020.

Unfortunately, coal gasification associated with combined cycle power generation still costs significantly more than pulverized coal-fired boilers with advanced steam turbines. Natural gas turbines, on the other hand, are forecast to take up more than 80% of new generating capacity in the United States over the next 10 to 15 years.

Typically, the current state of the art for natural gas-fuelled combined cycle power generation is a net thermal efficiency of about 60%, if the latest General Electric Series H (1500°C Class) gas turbine is used, for example. At this level of efficiency, direct natural gas firing for steel scrap melting inherently has an advantage over electrical heating by a factor of 1.67 times. Therefore, in very simple terms taking into account both the previous factor of 1.6 melting rate improvement for truly continuous versus batch charging and the energy savings introduced by avoidance of electric power generation, directly fired continuous steelmaking should score a rating of  $1.67 + 1.60 = 3.27$  times more in overall effectiveness in comparison with conventional EAF technology based on electricity from fossil fuel sources. In addition, the comparison must take into account one of the key features of truly continuous steelmaking, as pointed out previously, is the ability to accept highly contaminated scrap and produce high quality steel as well as a range of value-added nonferrous metal by-products. This potentially gives continuous natural gas-based steelmaking an unassailable competitive advantage.

Besides excelling in energy efficiency, any serious challenger to established EAF technology will need to demonstrate a high degree of flexibility. The technology must be capable of adapting to virgin iron units as well as superiority with respect to scrap charging. Continuous charging and new proposals for in-line processing of contaminated steel scrap are compatible with the desire to enhance flexibility, but still a case has to be made for scenarios in which scrap is just not available at the right price in the tonnages required. Accordingly in this discussion, it is worthwhile considering the principal natural gas-based alternatives to steel scrap, namely direct reduced iron (DRI) and hot briquetted iron (HBI). Many other alternate iron (AI) sources are currently being promoted especially those based on coal-based virgin iron ore reduction but these, although likely to vastly increase in importance in the longer term, are dwarfed by gaseous reduction, which, dominates the current AI scene. According to Midrex Technologies, world DRI output hit 43 Mt in 2000. Midrex Direct Reduction plants produced 68% of this total, HYL III 19.5% and all other technologies, including gas and coal based, made up the remaining 13%; DRI represented 83% and HBI 17%.

According to Voest-Alpine, HBI produced with their FINMET process reached a grand total figure exceeding 5Mt during 2003. At present HBI is compacted at temperatures in excess of 650°C, but for local proximity use, clearly the reduced material before briquetting could be fed directly at 650°C into the melting loop of the current proposal. In effect this would capture the benefits of integrated iron and steelmaking with both scrap and virgin iron units feeding the operation, depending entirely on economic considerations. Also of course, this is a very effective way of very substantially reducing greenhouse gas emissions.

In a melt circulation system, non-agglomerated reduced iron materials, such as FINMET, on being distributed across the width of a moving liquid iron surface will be immediately either “flash melted” or alternatively, larger material will be coated with a frozen layer of solidified iron bath material to form aggregates that will sink to the bottom of the bath, whilst undergoing transient heat transfer back to the melting point. By profiling the bath depth, melt circulation affords an appropriate mechanism to ensure that such material does not accumulate in the immediate vicinity of the charging location. By appropriate design and due attention to what is known as the “saltation velocity”, any solidified material can be swept downstream clear of the charging area, whilst it is being assimilated into the melt. Such phenomena are readily quantified and should proceed smoothly without the need for extensive piloting and development expenditure.

Alternate sources of iron, such as HBI and DRI, imported into a steelplant from a remote location in an agglomerated form, would be simply added to shredded steel scrap in whatever proportion dictated and should pass through a convective preheater without disruptive influence once due attention is paid to bed permeability issues and acceptance of the fact that flux requirements will need to be increased in order to slag the extra  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  introduced into the steelmaking system. At levels up to about 20%, EAF performance is claimed not to suffer unduly but at higher rates, electricity consumption increases significantly due to the lower metallization and higher gangue content of DRI/HBI. Typically, slag makes also increase significantly, approximately doubling for an HBI increase from 20 to 60%.

If climate change and global warming concerns reach crisis levels, it is reassuring to note that natural gas-based steelmaking, with proven commercial technology, could provide a rational way forward. BHP Billiton and Newcastle University workers in Australia have conducted Life Cycle Analysis studies for a range of steelmaking routes, which clearly show that natural gas combined cycle power generation coupled with a conventional EAF in close proximity to FINMET, as for a hypothetical plant at Port Hedland, W.A., based on N-W Shelf piped-in natural gas, has projected net greenhouse gas emissions of 1.42 t  $\text{CO}_2$ -e per tonne of cast steel compared with a net figure, after making allowances for slag and electricity credits, of 2.16 t  $\text{CO}_2$  e per tonne cast steel for integrated iron and steelmaking by the traditional route of blast furnace (B/F) and basic oxygen steelmaking (BOS). The differential would be enhanced even further if the EAF were replaced by a natural gas-fired continuous steelmaking system based on melt circulation.

Electric arc steelmaking with recycled steel scrap would be truly sustainable, if powered by electricity generated entirely from renewable energy resources. Of the various alternatives available, it is now proposed that such an ideal objective is most likely to be attainable by direct fuel firing based on pyrolysis of renewable carbonaceous materials as the prime energy source. Such carbonaceous materials could include, for example, metropolitan solid waste (MSW), biomass or scrap tyres. However, in the context of the present discussion a more direct linkage is already available, namely organic coated steel scrap.

The focus now is entirely on scrap-based steelmaking in more general terms. Accordingly, it is recognized that the clean metallic scrap referred to previously is unlikely to be available in the quantities needed to sustain a major steel complex with the same output of say 2 Mtpa as considered in the previous example. The non-ferrous metal

contamination may remain unchanged but now there is also a need to consider the more realistic case of scrap contaminated with plastics, wood, vegetable matter and possibly unconsumed food residues.

Ideally, the new continuous steelmaking process must be able to accept the aforementioned composite scrap input without attracting expensive pre-treatment charges or high labour-cost sorting as a pre-requisite to securing its financial competitive advantage. On the other hand, its environmental credentials must be superlative. The iron and steel industry must not get embroiled with the issues, which rightly or wrongly have been a major disruptive influence on the more widespread introduction of advanced incineration technology for the treatment of MSW and other more specialist waste arisings. Recyclability is steel's major asset and this most definitely must not be put at risk.

Because of the now anticipated contamination of the steel scrap with carbonaceous material as well as the non-ferrous metals considered previously, the protective gas atmosphere in the melting loop and scrap preheater is now recirculated pyrolysis gas as opposed to argon previously. Also now that the protective gas is being generated *in-situ* continuously, the need for a small bleed to remove accumulated impurities no longer exists, but rather superimposed on the massive circulation of protective gas as the vehicle for sensible heat transfer for scrap preheating, withdrawal of pyrolysis gas at a relatively small rate in comparison with that being recirculated must be undertaken at the same rate as it is formed. Provided issues related to prevention of dioxin formation are firmly in place within the protective gas recirculation system, there is no reason why the pyrolysis gas withdrawn from the scrap melting loop cannot be used to supplement the overall thermal demand involved in scrap melting. Under favourable conditions, a significant reduction in the amount of natural gas required is achieved by this mechanism.

Particular examples of the invention as applied to continuous steelmaking using contaminated steel scrap directly as feed will now be described with reference to the accompanying drawings in which:

Figure 1 relates to relevant prior art showing continuous steelmaking starting with virgin iron ore and coal in combination with three processing loops in series in which ferrous melt is force circulated in closed loops firstly one for ironmaking followed then by two for steelmaking in which oxygen is not permitted to directly contact iron-carbon melts at any stage.

Figure 2 summarizes in block diagram format the various sub-systems of the present invention for continuous oxygen steelmaking based on charging contaminated steel scrap with primary energy input from oxygen fuel combustion based on natural gas, synthesis gas, pyrolysis gases derived from biomass or solid waste arisings either associated with the steel scrap or independently generated, coke oven gas, blast-furnace gas or other primary ironmaking-derived fuel gas.

Figure 3 is an overall flow diagram of a steel plant in which the method of the present invention can be performed starting with scrap feed and finishing with refined liquid steel ready for continuous casting. It also represents the simplest case applicable to scrap with only a single non-ferrous metal contaminant at an appreciable concentration level.

Figure 4 shows a schematic arrangement in elevation and plan of two melt circulation loops which process preheated solid scrap, firstly in a melting loop, followed then by continuous liquid scrap withdrawal to vacuum desorbers arranged in parallel for stripping volatile non-ferrous metals or associated gaseous compounds using an appropriate strip gas, then discharging continuously into a steelmaking loop for adjusting the composition of the liquid steel to its product specification, both within the channel arms comprising the loop and in the associated RH-type degasser, which functions in a refining role as well as providing melt circulation.

Figure 5 shows a schematic arrangement of melt circulation loops and associated vacuum desorbers necessary to treat an unsegregated scrap charge containing relatively large concentrations of both copper and tin, which is to be refined to liquid steel in two steelmaking loops to a high purity product specification in advance of continuous casting.

Figure 6 is a sectional elevation and sectional plan view of a vacuum desorber with provision for radiative preheating of liquid scrap pumped up from the melting loop prior to its entry into the top of the reduced pressure packed bed contactor, in which liquid scrap irrigates the packing in counterflow to an upward rising strip gas.

Figure 7 shows an alternative method of preheating the liquid scrap referred to in Figure 6 using externally cooled current input connectors for an electrical conductive heating system comprising a horizontal strip channel of melt inside the vacuum desorber, arranged so that the channel remains full of liquid strip by controlling the rate of central discharge during operation, but empties out fully once supply is terminated. A sectional elevation and sectional end elevation are shown in this drawing.

Figure 8 illustrates the front or charge end of the argon/inert gas recirculating scrap-melting system.

Figure 9 is a schematic sectional elevation of the iron vapour condensation system.

Referring now to Figure 3 of the drawings, steel scrap 1 is deposited or charged continuously onto the lower submerged end of an inclined conveyor 2, which traverses upwards through a water bath (not shown) thereby creating a water seal between the surrounding atmosphere and the contents of an extensive gas-tight envelope comprising a horizontal conveyor system 3 heated from above by tubular radiators 4 to effect drying, preheating as well as pyrolysis of any organic material associated with the steel scrap. Initially the water-laden charge is dewatered as it falls from the inclined conveyor onto the horizontal conveyor and in addition optionally by an "air-knife" system or similar device located above the first section of the horizontal conveyor and based on cooled compressed argon, other inert gas or pyrolysis gas depending on the particular application and the nature of the charge material. The objective here is to remove as much liquid water as possible from the scrap and return it to the water bath before it enters the scrap preheating section.

Galvanized steel material is heated under benign non-oxidizing conditions so that the zinc or zinc alloy coating is "sweated off" as liquid zinc (melting point 420°C) and separated from scrap as it falls and then progresses along a vibratory screen/feeder 5 discharging scrap onto a second horizontal conveyor 6 whilst recovering molten zinc into a sump 7 for either intermittent or continuous tapping of a liquid zinc by-product 8. The scrap is further heated to

about 500°C as it progresses along the second horizontal conveyor 6, which discharges hot scrap via a chute 9 into the top of the convective reheater 10 comprising a moving packed bed of scrap material in which convective heat transfer is accomplished by countercurrent contacting with highly preheated argon/inert gas or pyrolysis gas.

Any aluminium associated with the scrap is melted (melting point 660°C) under benign conditions and trickles down to the bottom of the packed bed from where is separated from scrap using a trommel screen 11 or similar device to recover a molten aluminium by-product 12. The preheated scrap at about 900°C falls or is distributed onto the moving surface of the charge arm 13 of the melt circulation melting loop. The gas protective atmosphere extends right through this scrap preheating circuit from the charge arm just referred to back to the top of the convective preheater. Because pyrolysis of organic material may lead to increased levels of volatile organic compounds (VOC) as well as hydrogen chloride, it is important to balance the pressure in the radiative preheating zone and baffle the gas space effectively so that a small positive flow of cleaned recirculated gas is maintained as a purge from this zone rather than permitting infiltration of the contaminated gases emerging from the top of the convective preheater.

Returning to the protective gas atmosphere emanating from the top of the convective scrap preheater, this gas at about 550°C is recirculated in a closed loop system with a high temperature fan or gas booster 14 which discharges the possibly contaminated gas to a molten aluminium-based heat exchanger and chemical reactor system. This comprises a closed loop melt circulation arrangement with molten aluminium force circulated either with a gas lift RH-type system 15 or alternatively, by an electromagnetic liquid metal pump of the type now widely used in the secondary aluminium industry. One side 16 of the molten aluminium melt circulation loop receives heat from the hot gases emerging from the combustion arm 17 of the scrap melting loop to which is added a stream of cooler recirculated gas to moderate its temperature from around 1780°C to about 1100°C before its admission to the aluminium melt circulation loop. By covering the surface of the molten aluminium on the heat input side 16 with a thin layer of molten cryolite-based flux and ensuring that conditions are maintained so that oxidation is virtually precluded, the temperature of the combustion gases is reduced from the above figure of 1100°C to about 1000°C during passage over the flux covered surface. This heat input is picked up by the circulating molten aluminium and transferred on the other side of the loop 18 to the incoming recirculating protective gas atmosphere so that its temperature is raised from around 550°C to about 950°C using an adaptation of commercially well proven technology, initially developed in the U.K. as the basis of the then new zinc blast furnace, the Imperial Smelting Furnace (ISF), employing what has now become known as a mechanical rotor splash system. Mechanical rotors just dipping into a pool of melt throw up a vast amount of mechanical spray into the gas space above providing a very large gas/liquid interfacial area, ideal for intensive heat and mass transfer. The two chemical reactions of prime significance between molten aluminium and recirculating protective gas are those involving the removal of both hydrogen chloride and water vapour from the gas phase.

The overall chemistry can be expressed by Equations 3 and 4:

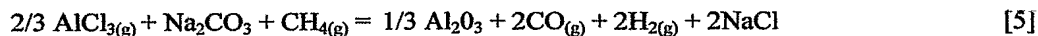




Dross removal systems are well developed for an ISF condenser, but unlike zinc oxide dross floating on the molten lead within an ISF condenser, aluminium oxide generated by reaction [3] is more likely to sink to the bottom of the aluminium pool so its periodic removal will need further development, perhaps it is worth noting that the aluminium industry already has available technology for batch-wise siphoning out molten aluminium from beneath top layers of molten cryolite in its universally established reduction cell production technology so an extrapolation of this for the present purposes would seem a logical basis for initial evaluation. Because both reactions [3] and [4] are highly exothermic, the provision of intensive heat and mass transfer as secured by the mechanical splash rotor system is beneficial and even small amounts of gaseous hydrogen chloride and residual water vapour in the protective gas being recirculated can have a significant positive impact on the overall heat balance, but this of course has to be balanced against the consumption of aluminium metal and the costs of removing oxide from metal implied in such a scheme.

The gas emerging from the aluminium splash system containing variable amounts of aluminium chloride in the gaseous state depending on the chloride content of the original scrap feed as well as the associated hydrogen reaction product is next scrubbed free of halide content by chemical reaction with sodium carbonate contained in a binary melt with sodium chloride in a countercurrent gas/liquid contactor 19 probably of the fixed packed bed type to which is added a solid feed of soda ash or the naturally occurring mineral trona 20. A slurry of aluminium oxide dispersed in the binary fused salt is removed from the bottom 21 either continuously or intermittently depending on the level of halide contamination, for subsequent downstream processing for alumina and salts recovery.

In the absence of natural gas admission to the inlet gas to the fused salt scrubber, the chemical reactions involving carbon dioxide formation are exothermic but by adding natural gas the carbon dioxide reforming reaction with natural gas absorbs this heat leading to a slight thermal deficit, if the natural gas added is partially oxidized to carbon monoxide and hydrogen by the reforming reaction. However, because the amount of heat absorbed if natural gas is added stoichiometrically is relatively small, this thermal effect is virtually swamped by the total enthalpy of the protective gas itself, so the gas leaves the scrubber at around 950°C for transmission to the base of the convective scrap heater 10 in a virtually halide-free condition. The overall chemistry involved is given by Equation 5.



The combustion gases leaving the heat input side 16 of the aluminium melt circulation loop at about 1000°C provide the thermal input to the tubular radiative system 4, which supplies the energy requirements for radiative charge preheating to about 500°C, zinc melting, pyrolysis of organic components associated with the charge scrap as well as the initial drying out of residual water retained by the scrap feed after de-watering. The exit gas at 22 can be used for fuel gas and oxygen preheating separately and to supplement thermal requirements associated with electricity generation, if so required.

Liquid scrap is pumped using inert gas injection from the melting loop by an air-lift type system 23 to the top of the vacuum desorber 24, optionally via an external high-level sump 25 incorporating radiative heating elements to raise the liquid scrap temperature up 1780°C or thereabouts to facilitate stripping of copper or stannous sulphide from the liquid scrap into the strip gas. The refined liquid scrap is removed continuously from a low-level sump 26 at near

atmospheric pressure by a siphon 27 to a liquid steel melt circulation loop comprising two arms 28 and 29, probably open channels, for desulphurization and dephosphorization, if needed, as well as final composition adjustment using both the RH 15 and the two arms 28 and 29 for these purposes. Liquid steel is removed either continuously or intermittently at 30 for transmission to a continuous casting facility, it being recognized that there is adequate melt storage capacity in a melt circulation loop to absorb interruptions to continuity.

Referring now to Figure 4 of the drawings, the arrangement shows the disposition of a bank of four vacuum desorbers 24, each typically about 4 m in diameter, arranged in parallel in between the scrap melting melt circulation loop with arms 13 and 17 and a liquid steel loop with arms 28 and 29 each containing an RH 15 and a melt circulation siphon 31. Liquid scrap is pumped to the top of the desorbers by "air-lift" type pumps 23 discharging optionally into high level sumps 25, if radiative heating is employed to raise the liquid scrap temperature prior to its admission to the top of the packed beds inside the desorbers. The product steel siphons 27 continuously transfer the liquid steel from each of the vacuum desorbers 24 via the low-level sumps 26 to the steel melt circulation loop with arm 28, from which product liquid steel can be withdrawn either intermittently or continuously to a continuous casting facility (not shown).

Referring now to Figure 5 of the drawings, this embodiment shown depicts a steel plant in which the method of the present invention can be performed to recover continuously a liquid steel product with a high grade purity specification from unsegregated scrap containing appreciable levels of both copper and tin contamination. The scrap melting loop, air-lift type pump and the first vacuum desorber are identical to those described in Figure 4. This first vacuum desorber is where copper is removed but little elemental tin is desorbed into the strip gas. For clarity, only the second in-line "air-lift" pump and vacuum desorber are marked accordingly in this figure. A sulphur containing gas is used as the lift gas for the "air-lift" pump 23 and is injected at 32 or alternatively the sulphur requirements for stannous sulphide volatilization in the vacuum desorber 24 are injected into the liquid scrap in the high-level sump 25 in advance of or during transmission of the melt to the top of the backed bed inside the vacuum desorber. For this particular case, because a high purity specification for the steel product is demanded, two steel melt circulation loops are provided with arms 28, 29, 32 and 33. Final high-grade liquid steel product is withdrawn either continuously or intermittently via 34 for transmission to a continuous casting facility as before.

Referring now to Figure 6 of the drawings, this shows one of the alternative options for elevating the liquid scrap temperature prior to its admission to a vacuum desorber 24 as well as details of the arrangement of the desorber internals in terms of refractory linings and provision of the submerged entry means 35 for admission of liquid scrap to the central raised overflow port 36 for discharge and distribution of high temperature liquid scrap onto the top of the packing elements (not shown) within the desorber. Liquid scrap arrives at the upper-level sump 25 via the upleg 38 of the "air-lift" type pump from the scrap melting arm 13 with its exit 39 not submerged in the liquid scrap maintained as a pool 37 by the centrally located and raised overflow spout 36. Radiation to the free surface of this pool of liquid scrap from the bank of graphite heater electrodes 40 arranged above the melt provide the energy input to raise the temperature to an appropriate elevated level, typically 1780°C, prior to its admission to the vacuum desorber 24 via the crossover channel 35 and ultimately to the top of the packed bed via the overflow port 36. It is important to design this arrangement so that a minimum depth of liquid scrap is maintained above the refractory hearth of the upper-level sump 25 to preclude growth of carbon monoxide bubbles on gas cavities in the hearth

refractory in order to control carbon monoxide evolution through the gas liquid interface and the resultant splashing of liquid scrap onto the graphite heating elements not only to preserve their integrity, but also to prevent unnecessary carbon pick-up into the melt.

Careful consideration needs to be directed at accommodating differential thermal expansion throughout this system and one such option is to arrange for the high-level sump 25 and its contents to be supported by tracked rollers 41 as shown, or other appropriate means. Special mention also needs to be made to the very high liquid scrap temperatures involved and the need for careful selection of high performance refractory materials throughout the top region of the desorber 24 and within the upper-level sump 25. This is especially the case for the overflow spout 36 and its associated tundish, in which the second pool 42 of very high temperature liquid scrap is maintained. Again careful consideration will need to be directed towards means for accommodating differential thermal expansion in this region. Also it is desirable to provide means for removal of the overflow spout 36 from setting in the hearth of the tundish, when production is stopped, to ensure that a pool of liquid steel does not remain in either of the liquid pools 37 and 42 and eventually freeze over. This precaution is to avoid damage to the refractory and ceramic linings when the solidified steel is reheated when operations are to recommence after a prolonged shutdown. For shorter duration stoppages, steps need to be taken to ensure that the liquid pools 37 and 42 do not freeze over. This is straightforward enough for the pool 37 within the upper-level sump by reason of the existence of the bank of graphite heating elements 40. However, some electrical heating, either conductive or radiative (not shown), needs to be installed within the top region of the desorber 24 to prevent a freeze-up from occurring in this area.

Referring now to Figure 7 of the drawings, this shows a preferred option for elevating the liquid scrap temperature prior to its admission to a vacuum desorber 24 as well as the detailed refractory and ceramic component arrangement. From the outset attention is directed to the perforated arched refractory construction 43 involved in providing a fully supported strip 44 of very high temperature liquid scrap undergoing electrical conductive heating by direct passage of a heavy electrical current through the limited cross sectional area of the liquid strip contained within a channel 45 set within the refractory arch. The perforations are to provide low pressure drop strip gas flow from the packed bed (not shown) below within the desorber 24 to the gas off take 46 leading to the reduced pressure strip gas recirculation means (not shown) and also its associated vacuum pumping arrangement to maintain the desired reduced pressure in the recirculating strip gas loop by leading off a small fraction of the strip gas for removal of gaseous infiltration into the reduced pressure circuit. As in float glass technology for provision of a protective gas atmosphere in the float chamber, an appropriate level of hydrogen is maintained within the strip gas to react with infiltrated oxygen and thus prevent oxidation of the liquid steel or being instrumental in causing uncontrolled evolution of carbon monoxide within the desorber and its ancillaries.

The liquid strip constituting the circuit for electrical conductive heating is maintained at a predetermined depth by the control rod assemblies 47 depicted schematically in the drawing. Also shown is the low-level liquid sump 26 into which the downflow of liquid steel product is accommodated, in this example by an upleg and a downleg from the reduced pressure desorber 24 in order to induce melt circulation by RH action between the vacuum desorber 24 and the low-level sump 26, which is maintained close to atmospheric pressure. This melt circulation is to combat perceived difficulties in withdrawing continuously the relatively small product flowrate of liquid steel in the face of possible excessive carbon monoxide evolution, which may occur if a single offtake without melt circulation were

used, as discussed more fully elsewhere in the description of this invention. Whether or not this enhancement is really necessary would depend on the particular concentration levels of dissolved carbon and oxygen in the liquid steel at this juncture and is thus subject to a measure of control by the process operator.

The electrical current input to conductively heat the strip of liquid scrap within the desorber is achieved by cooling the exposed external steel sections of the strip 50 and 51 in direct contact with liquid steel at the liquidus temperature well removed from the high temperature region itself but part of the same physical and electrical circuit, fashioned so that the exposed ends can be sealed using conventional vacuum technology practice to afford a means for connection to the AC electrical power supply. A variable low voltage heavy current transformer arrangement will be used for this purpose with possible phase balancing by interconnection of adjacent units to form an overall supply circuit.

It will be appreciated that the concerns about melt freeze-up expressed in the discussion of Figure 6 do not apply with this option. Electrical conductive heating provides the solution to the freeze-up problem. Also it must be stressed that the liquid scrap arriving by the "air-lift" upleg will need to have its inert lift gas bled off before the liquid scrap enters the channel 45 and means for this will have to be provided (not shown in this schematic diagram). The liquid steel progressing to the next step in the continuous process is removed from the lower-level sump 26 by the product siphon 27 as shown in the drawing.

Referring now to Figure 8 of the drawings, this shows a simplified schematic arrangement for preheating clean scrap without organic contamination and without the necessity to recover an intermediate zinc by-product. The preferred inert gas is argon as no pyrolysis gas is formed in the system and the only real concern is water vapour pickup after physical de-watering (not shown) to remove excess liquid water. Scrap 1 is charged through the water seal 52 onto the inclined conveyor 2, which after passage through the water seal 2 discharges its scrap load onto a single horizontal conveyor 3. After initial de-watering (not shown) the scrap passes under a bank of tubular radiant heaters 4 so that its temperature is gradually raised to about 500°C before discharge into the top of the scrap convective heater 10. The principal gas offtake for the closed loop argon recirculation system is at 53, which leads to the high temperature fan or booster for argon recirculation and the closed loop melt circulation system employing molten aluminium both as a heat transfer medium for preheating the argon to about 950°C while comprehensively reducing the water vapour content of the argon before its entry into the base of the convective scrap preheater 10. In this convective scrap preheater the scrap is preheated under benign non-oxidizing conditions without yield loss to about 900°C before admission to the scrap melting arm of the scrap melting melt circulation loop.

A small purge of argon is taken off at 54 to a gas purification system in order to control the build-up of nitrogen in the recirculating argon system. As the protective gas atmosphere extends right through to the melting loop, it is desirable to avoid problems with nitrogen absorption into the liquid steel by tightly controlling its build-up by these means. Nitrogen contamination of the argon arises from air infiltration throughout the system but principally associated with the scrap charged containing inaccessible porosity, which is not displaced by water as the charge material progresses through the water seal. The associated oxygen reacts in the liquid aluminium splash system used for argon preheating and therefore problems with oxygen build-up and steel yield losses due to oxidation do not arise with the system under discussion.

Referring now to Figure 9 of the drawings, iron vapour saturated strip gas 55 from the vacuum desorber enters the condenser through a number of ceramic pipes 56 extending through an annular packed bed 57 to the gas space beneath the bed 58. Liquid iron 59 close to its liquidus temperature is forced to irrigate the packing using a gas lift principle with the inert gas 60, probably argon, being injected from the top again by a number of ceramic pipes 61. The whole assembly is formed by utilizing the residual unmelted steel shell 62 and electrical conductive heating approach advocated by the applicant in International Publication Number WO 2004/007778 A1, which relies on heat extraction from liquid steel already close to its liquidus temperature, using computer assisted location of steam raising tubes 63 such that the desired thickness of retained unmelted steel is maintained at the appropriate location. Clearly, liquid steel close to its liquidus temperature is an ideal medium for ensuring highly efficient condensation of iron vapour without effecting to any significant extent copper or stannous sulphide vapour condensation so that these pass through the condenser in an unchanged condition. This is the fundamental basis of the selective recovery of copper and tin without undue losses to iron condensate and is only a realistic option for a truly continuous steelmaking process of the type identified in the present invention. Finally, the strip gas offtake from the iron vapour condenser to the copper condenser is shown at 64.

#### EXAMPLE

Further consideration of steel scrap charging in the context of primary iron and steelmaking will now be given. In this illustrative example 2 Mtpa steel is produced from 500,000 tpa Fe virgin and 1,500,000 tpa Fe scrap.

Some calculated parameters have been evaluated for the key plant items relating to the single point introduction of liquid scrap into the primary continuous steelmaking circuit for a 2 Mtpa total steel case. For this particular case, an overall heat balance on the scrap-melting loop, fired by post combustion of gases generated initially during ironmaking from virgin materials in the ironmaking loop, is given in Table I.

To retain comparability in the cases being considered, it was decided to base calculations on the availability of a given vacuum pumping system. It has been assumed that the vacuum pumping plant is the same as that reported for a Recirculating Degasser (RD) with a Kawasaki Top Blowing (KTB) lance (D.V. Barradell, P. Dawson, R.I. Blake and C. Priday: *Iron and Steelmaker*, July 1995, pp. 29-34). This vacuum system consists of a three-stage steam ejector combination with inter-condensers and three high vacuum water-ring pumps that act in parallel as the atmospheric pumping stage. The RD-KTB Degasser pumping capacity in terms of dry air equivalent is given as 1,500 kg/h at 0.5 mbar; 1,700 kg/h at 0.67 mbar and 9,000 kg/h at 200 mbar.

The next consideration is specification of the operating pressure of the actual desorption step. In the present case, a realistic inlet pressure of 3 mbar has been arrived at, based on estimates of the gas phase pressure drop between the vacuum pumping system and the desorber, bearing in mind the necessity for iron vapour condensation, followed then by possibly two stages of copper condensation, with the first condensate being reverted back to the liquid scrap feed and only the final copper condensate being removed continuously as a liquid via a barometric leg to yield ultimately a high quality copper ingot as a by-product.

Further consideration is then needed concerning the likely availability of a particular type of scrap and the degree of flexibility in processing options required to safeguard economic viability at sometime in the future. It is suggested that this is realized by actively seeking out the then current most competitive mix of iron units as feed to the continuous steelmaking circuit. As an example, let us consider, that three desorber units in parallel can be serviced by the specified vacuum system. Table II summarizes some key design parameters for one desorber in such an arrangement. Table III gives an example of the expected performance for a single desorber 6 m in diameter when treating either a typical copper or tin contaminated continuous liquid scrap stream.

**Table I. Overall Heat Balance on Scrap Melting Loop (Ideal, No Heat Losses)**

Basis: 3 tonnes scrap per 1 tonne virgin iron

<u>Input</u>	<u>Temperature °C</u>	<u>Amount kmol</u>	<u>Total Enthalpy MJ</u>
CO	1980	1.797	- 80.70
H <sub>2</sub>	1980	0.143	8.79
H <sub>2</sub> O	1980	17.081	- 2,661.50
CO <sub>2</sub>	1980	38.122	- 10,946.91
O <sub>2</sub>	1980	2.112	145.33
Preheated scrap	924	53.571	<u>1,898.90</u>
			<u>- 11,636.12</u>
<u>Output</u>			
CO	1542	0.069	- 4.22
H <sub>2</sub>	1542	0.008	0.37
H <sub>2</sub> O	1542	17.216	- 3,070.97
CO <sub>2</sub>	1542	39.850	- 12,530.80
O <sub>2</sub>	1542	1.180	61.64
Liquid scrap	1536	53.571	<u>3,907.64</u>
			<u>11,636.34</u>

Desorption of non-ferrous metal impurities in liquid scrap can be readily achieved in-line with continuous steelmaking based on melt circulation. Around three tonnes of scrap can be processed per one tonne of virgin iron. Galvanized and organic-coated scrap feeds can be preheated in a recirculating argon system to sweat out metallic zinc as a by-product with the remaining zinc simply eliminated from the liquid scrap by physical desorption at atmospheric pressure.

For copper and tin contamination, the liquid scrap can be refined in-line with copper being recovered continuously to yield immediately a high quality ingot copper as a by-product. For tin-contaminated liquid scrap, sulphur must be added and stannous sulphide desorbed. After condensation of iron then copper, the tin sulphide vapour can be absorbed in molten tin, for example, with metallic zinc addition to regenerate metallic tin in a closed loop system producing a low-iron zinc sulphide by-product and the liquid metal overflow cast into tin ingots also as a by-product.

It can be shown (N.A. Warner: *Metallurgical and Materials Transactions B*, August 2004, Vol. 35B, 633-674) that a typical RD-KTB vacuum pumping system is capable of simultaneously refining:

0.5 Mtpa liquid scrap containing 0.4% Sn down to 0.02% Sn at 2.5 mbar pressure

0.6 Mtpa liquid scrap containing 0.5% Cu down to 0.05% Cu at 2.5 mbar pressure

0.4 Mtpa galvanized scrap from 1% Zn down to 5 ppm Zn at atmospheric pressure.

**Table II. Vacuum Desorber - Key Parameters**

Liquid scrap throughput	500,000 tpa
Internal diameter	6.0 m
Nitrogen strip gas	567 kg/h
Inlet pressure	3 mbar
Outlet pressure	2 mbar
Inlet liquid scrap temperature	1780°C
Outlet liquid scrap temperature	1671°C
Liquid scrap mass velocity (L)	0.561 kg/s m <sup>2</sup>
Volumetric flux of irrigant (L <sub>0</sub> )	7.98 x 10 <sup>-3</sup> m <sup>3</sup> /(s) m <sup>2</sup>
Absissa (L/μ)	101.6 m <sup>-1</sup>
Liquid-phase Schmidt Number (Sc)	160
Packing elements	300 mm Raschig rings
Characteristic dimension (d <sub>s</sub> )	0.434 m
Gas superficial velocity (mean)	16.7 m/s
Bed voidage	0.74
Mean true gas velocity (v <sub>g</sub> )	22.5 m/s
Mean gas density for composite feed	5.33 x 10 <sup>-4</sup> kg/m <sup>3</sup>
Absissa (v <sub>g</sub> ρ / μ)	201 m <sup>-1</sup>
Ordinate for liquid-phase mass transfer	0.20
Ordinate for gas-phase mass transfer	1.22 or 0.72
Estimated H <sub>L</sub>	1.10 m

**Table III. Vacuum Desorber Performance***Liquid Scrap containing Copper*

Gas-phase Schmidt Number (Sc)	0.74
Estimated H <sub>G</sub> and H <sub>OG</sub>	
(a) correlation including zinc absorption	3.12 m and 3.57 m
(b) correlation excluding zinc absorption	1.56 m and 2.01 m
<b>Nominal Liquid Scrap Throughput</b>	<b>300,000 tpa</b>
Estimated N <sub>OG</sub> (0.5% Cu → 0.05% Cu)	3.46
(a) packed height required	12.38 m
(b) packed height required	6.97 m

**Mean Packed Height** **9.68 m**

*Liquid Scrap containing Tin*

Gas-phase Schmidt Number (Sc)	1.23
Estimated H <sub>G</sub> and H <sub>OG</sub>	
(a) correlation including zinc absorption	4.39 m and 5.69 m
(b) correlation excluding zinc absorption	2.19 m and 3.50 m
<b>Nominal Liquid Scrap Throughput</b>	<b>500,000 tpa</b>
Sulphur addition	1.5 x Stoichiometric
Estimated N <sub>OG</sub> (for 0.4% Sn – 0.02% Sn)	1.94
(a) packed height required	11.04 m
(b) packed height required	6.79 m

**Mean Packed Height** **8.92 m**

The engineering feasibility for steelworks of the future to take in scrap feedstocks with only simple physical segregation at point of origin has been demonstrated theoretically by detailed fundamental analysis of the various mass and heat transfer aspects. Present day vacuum degassing pumping systems can be adapted without further

development to yield a viable solution to what has been regarded by many as a serious impediment to increasing the amount of steel scrap recycled in the future. This can all be achieved without concern about the build-up of tramp elements. Above all, it stems directly from the projected development of truly continuous integrated iron and steelmaking and also natural gas fired continuous steelmaking from scrap, which is highlighted in this invention.

It does, however, rely heavily on development of conductive heating to raise the temperature of liquid scrap from around the liquidus temperature perhaps to levels approaching the limits of conventional refractories. In this regard it should be noted that the partial pressure of tin sulphide at a given level of sulphur in liquid scrap is reduced by a factor of 2.24 if the temperature is reduced to say 1600°C from 1780°C. Even more dramatically, the vapour pressure of copper is decreased by a factor of 5.74 over the same temperature range.

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In the afore-mentioned example, a typical vacuum pumping system such as that associated with a recirculating degassing system was assumed to exist in an established steelmaking site, but in a preferred embodiment at a greenfield site for example, stripping volatile impurities from liquid scrap into a reduced pressure gas does not need the energy and cost penalties associated with compressing the strip gas at say 1 mbar level to discharge at atmospheric pressure. A far better approach is to recirculate the strip gas in a closed circuit once the contaminants have been removed either by physical or chemical means. Under these conditions the vacuum system pressure ratio rather than being in the region of 1000 to 1 is reduced down to be no more than say 5 to 1 or even less. Accordingly, to a first approximation the theoretical energy consumption is thus reduced by a factor of  $\ln(1000/5)$  equals 5.3 if both compressions are conducted under isothermal conditions and about 15.8 for the usual industrial case of polytropic compression at say a polytropic efficiency of 80% for a diatomic strip gas, such as nitrogen, if multistage compression from the reduced pressure region back to atmospheric pressure is undertaken without heat dissipation between stages.

Electric arc steelmaking with recycled steel scrap would be truly sustainable, if powered by electricity generated entirely from renewable energy resources. Not surprisingly, it is now proposed that such an ideal objective is more likely to be attainable by direct fuel firing based on pyrolysis of renewable carbonaceous materials as the prime energy source. Such carbonaceous materials could include, for example, metropolitan solid waste (MSW), biomass or scrap tyres. However, in the context of the present paper a more direct linkage is already available, namely organic coated steel scrap.

In the U.K. it has been estimated that in excess of 1 Mtpa of organic coated scrap was generated in 2000. Organic coated steels are used both in the building and manufacturing sectors and the demand for both organic and metallic coated steels has increased dramatically in recent years. It has been suggested (R.W. Weaver, J. Edmundson and K. Williams, *Ironmaking and Steelmaking*, Vol. 26, No. 4, August 1999, pp. 285-290) that a possible way of recycling coated steels would be to separate the scrap into its component parts i.e. steel, zinc and organics, thereby allowing clean steel scrap to be available for existing steelmaking technology. On the other hand, if the obvious environmental concerns about volatile organic compounds (VOC) and the possible generation of extremely toxic dioxins and furans could be overcome in a cost effective manner, then it would seem perfectly logical to use the



inherent fuel values of such materials directly in our case to melt steel scrap, supplemented with natural gas, if so required.

There already exists a vast pool of technical knowledge and commercial know-how, which could be harnessed to accelerate the development of sustainable steelmaking along the lines of the aforementioned approach. In particular, MSW treatment with what is known as Thermoselect high temperature gasification technology would appear to be highly relevant in the present context. MSW has a low density and requires a great deal of space. The Thermoselect Process compacts this material to about 10% of its original volume using standard in-line scrap metal processes to produce highly compressed packets of waste which are pushed mechanically directly into an externally heated pyrolysis channel where the material is thermally cracked in the absence of air to form hot carbon packets and gaseous compounds, principally water, carbon monoxide, carbon dioxide, hydrogen and hydrocarbon gases. Although electricity generation is not the prime objective as it is in the Thermoselect Process, it could be advantageous to use the pyrolysis gas originally formed and the carbon packets with their associated metallics in a continuous steelmaking process. However, it is worth noting that the gases ultimately leaving the gasification zone in the Thermoselect Process are rapidly cooled in the absence of oxygen to avoid “de-novo” (new formation) synthesis of dioxin and furan compounds.

Organic coatings for external building applications are typically of the order of 200  $\mu\text{m}$  in thickness as opposed to 10 – 25  $\mu\text{m}$  more typical for internal cladding purposes. Weaver et al. (R.W. Weaver, J. Edmundson and K. Williams, *Ironmaking and Steelmaking*, Vol. 26, No. 4, August 1999, pp. 285-290) have demonstrated that heating PVC coated steel up to 200°C results in polymer degradation, achieving a decrease in molecular mass of around 70,000 without release of significant VOC, indicating that with thermal treatment the polymer chain is broken down to a less complex organic compound by the time it has reached 200°C. If PVC is heated at 5°C/min (i.e. relatively slowly) to say 500°C in an inert gas atmosphere, thermal degradation of the polymer chain continues and all the contained HCl is removed by the time the temperature reaches 700 K, but the maximum rate of dehydrochlorination in nitrogen occurs at 568 K (F. Tailoka and D.J. Fray: *Mineral Processing and Extractive Metallurgy (Trans. Inst. Min. Metall. C)*, 1997, Vol. 106). Using chromatography they demonstrated that the main hydrocarbons released to the gas phase included methane, ethane, propylene, propane and n-butane.

Because substantial amounts of HCl could be evolved in the thermal degradation of PVC plastic materials associated with contaminated steel scrap, the potential threat of possible emission of dioxins must be addressed. According to Nippon Steel's 2003 Annual Report, they have developed technology to overcome dioxin emissions in the exhaust gases of electric arc furnaces as well as in waste pyrolysis. Their direct waste melting and recycling system uses rapid gas cooling equipment (termed “trombone gas-coolers”) followed by resin-based filters and bag filters. This is effectively so-called “end of the pipe technology”. For continuous steelmaking using contaminated scrap, however, it would seem better to develop technology that deals with the potential hazards of dioxin emissions within the process itself. This approach will now be explored and appropriate technology identified as a further component of the method of recovering steel from contaminated scrap.

Chlorine must be present for dioxins to form in industrial processes and it can be generally stated that increased chlorine concentrations in feed materials enhance the prospects of dioxins formation and thus the prospects for very

harmful emission scenarios. In the present case if the steel scrap charged to the new process contains organic coated steel based on PVC, the hydrogen chloride evolved on pyrolysis needs to be removed from the pyrolysis gas to a very large degree within the process before attempting to recover its fuel energy content. For the present invention this is accomplished by contacting the gas emerging from the aluminium splash contacting system which results in volatile aluminium chloride gas being generated along with a small amount of residual hydrogen chloride, in a packed bed trickle-irrigated with a fused salt system that preferably fluxes or wets the entire packing surface and contains at least one chemical compound that is capable of reacting with and absorbing gaseous chlorine-containing gases, such as aluminium chloride or indeed residual hydrogen chloride that escaped reaction in the aluminium splash system.

A preferred reagent for this chlorine scrubbing system, which is readily available commercially and thus inexpensive, is sodium carbonate (soda ash) or perhaps the naturally occurring mineral, "trona". This is thermodynamically capable of removing both gaseous aluminium chloride and hydrogen chloride down to very low levels in the carrier gas. The sodium chloride which is one of the products of reaction is miscible with sodium carbonate in all proportions below 858°C in the fused salt binary system, which percolates by gravity through the packed bed countercurrent to the upward flow of pyrolysis gas as the continuous phase. The binary system forms a eutectic at 642°C, while sodium chloride itself has a melting point of 801°C. Below the eutectic the reaction between gaseous hydrogen chloride and sodium chloride is known to be inhibited by the formation of a dense impermeable and thus protective layer of the reaction product (sodium chloride), which prevents gaseous diffusion into and away from the reaction interface. In this invention this problem does not arise because of the formation of a liquid phase of eutectic melt composition, which is no longer capable of inhibiting reaction and is capable of continuing reaction until virtually all the contained sodium carbonate is fully consumed or alternatively the temperature falls below the solidus temperature, which is unlikely to happen because the chemical reactions involved are strongly exothermic.

Continuous refining of steel under reduced pressure in the afore-mentioned relatively sophisticated systems is inherently beset with the same fundamental problems that have foiled attempts to introduce continuous steelmaking at atmospheric pressure many times in the past. In this context, the current applicant drew attention to Bessemer's statement made in his autobiography, in which he refers to the steel melt as "a volcano in a veritable state of eruption" (N.A. Warner: *Proc. Yazawa Int. Symp. On Metallurgical and Materials Processing*, 132<sup>nd</sup> TMS Annual Meeting, San Diego, CA, March 2-6, 2003, vol. 1, pp. 881-900, TMS Warrendale, Pa.). This is known to be due to the sub-surface nucleation and rapid growth of carbon monoxide bubbles and their explosive passage as they burst through the gas /liquid interface accompanied by the generation of droplets and microspray, which then react violently with the gaseous environment. The problem is exacerbated under reduced pressure, so although counter-current gas treatment of metallurgical melts has been patented by the applicant in UK Patent GB 2 193 957 B, molten steel is not a quiescent melt of the type referred to in this former patent, which was directed at inactive melts, such as molten copper sulphide matte containing harmful impurities such as arsenic, antimony, bismuth and lead.

The problems with attempting to effect in-line continuous vacuum degassing of molten steel based on a steel flow equivalent to the desired steel production rate without massive recirculation of the molten steel have been well-documented in accounts of British Iron and Steel Research Association (BISRA) unsuccessful bid during the early 1960's to commercialize such a process. On the other hand, recirculating degassers, developed initially by Ruhrstahl-

Hereaus (RH) in the late 1950's and early 1960's, overcame the inherent problems by massive circulation of melt relative to the actual small throughput rate of steel production. The plant described in UK Patent GB 2 193 957 B clearly resembles RH vacuum degassing technology in terms of melt throughput with most of the melt exposed to the strip gas many times as it is circulated between the reservoir vessel containing up-leg and down-leg snorkels and the reduced pressure contacting vessel located immediately above. Accordingly, to apply this technology to in-line continuous processing of a non-quiescent melt as now required, demands provision of features not included in the former patent in recognition of the disruptive effects of carbon/oxygen interaction and carbon monoxide evolution.

The explosive disintegration of a steel stream containing dissolved carbon and oxygen as it enters a reduced pressure region, was studied by the applicant some years ago (N.A. Warner: *Journal of Iron & Steel Institute* (London) 1969, Vol. 40, 44-49). These experiments give an insight into conditions, which are totally non-conducive to continuous processing. It is clearly impossible for liquid scrap to progress from one stage to the next in-line to effect continuous removal of contaminants in liquid scrap under reduced pressure conditions in a flow circuit, whilst-ever the carbon/oxygen reaction is uncontrollably actively in progress.

State of the art with recirculating degassing for molten steel these days uses circulation rates, which are typically of the order of 200 t/min. However, in the early days of RH process development, melt circulation rates as low as 20 t/min were being used commercially to vacuum degas un-killed steel without prior deoxidation. Fuji Iron and Steel were the first to develop such a method for treating low carbon steel in undeoxidized open heats, when they installed RH vacuum degassing not merely to remove dissolved hydrogen but also to effect decarburization and deoxidation simultaneously. Therefore, a melt circulation rate of 20 t/min has been commercially demonstrated as a means of overcoming difficulties associated with transporting a carbon and oxygen containing steel melt through a barometric seal, also known as a barometric leg, from a vacuum back to atmospheric pressure for conditions typical of the then Fuji RH operation, which pertain to before degassing melt analyses of 0.055% carbon and 500 ppm oxygen with internal diameters of 200 and 150mm for the upflow and downflow snorkels, respectively and a circulation rate of 20 t/min.

If this 20 t/min were the actual flow of product liquid steel, it would equate to an annual production in excess of 10 Mtpa. However, the energy consumption implications of raising such steel throughputs from close to the liquidus temperature up to say 1700°C or even higher on a once through basis in order to volatilize copper and tin would be enormous and totally unacceptable for a plant producing steel products at a rate of say 0.5 Mtpa. The scheme outlined in UK Patent GB 2 193 957 B is thus unworkable for active melts such as those produced initially in all current steelmaking operations, unless completely back-mixed reservoir vessels or liquid sumps are provided with product rate inflow and product rate overflow or withdrawal, are located throughout the flow circuit, whenever molten steel is to be transferred from a low pressure region to the next in-line processing stage. However, countercurrent contacting, constrained by the limited height possible with a vacuum lift as proposed in the former patent, in any event does not provide anywhere near the height requirements necessary to achieve the extent of refining for the once through contacting, implicit in continuous processing to remove copper and tin from contaminated scrap.

Also as a direct consequence of backmixing in a recirculating system, the driving force for mass transfer at the top of the contactor is limited to that induced by the exit concentration of refined melt leaving the reservoir vessel, whereas for a once-through or in-line countercurrent contact without backmixing the driving force at the top of the contactor is many times greater as it reflects, in the present case, the relatively high inlet concentrations of copper and tin in the scrap feed material.

Furthermore, to achieve the specified removal rate of the volatile impurity (copper and tin in the present case) demands a certain partial pressure of the stripped element in the strip gas leaving the contacting system and in the limit this partial pressure cannot exceed the equilibrium condition between the melt at the top of the contactor and the strip gas leaving this region. Obviously, a backmixed system requires many more times the flow of strip gas and this coupled with the massive recirculation flow rate likely to be involved in the present case (say 20 t/min) would require a tower of vast internal diameter to avoid flooding. Clearly, the teachings of UK Patent GB 2 193 957 B are thus completely unworkable for the countercurrent treatment of liquid scrap with a strip gas under reduced pressure for the continuous removal of non-ferrous metal contaminants.

Attention also needs to be directed to ensuring that the gas-lift pumping systems required to elevate the liquid scrap to the top of the reduced pressure desorption towers is not adversely affected by excessive carbon monoxide evolution. Some carbon monoxide released in the upleg of an RH is seen as a positive contribution to the gas flow required to effect high circulation rates. However, a gas-lift pumping device demands the liquid phase to be the continuous phase and ideally, for homogeneous two-phase flow, the gas should be dispersed uniformly throughout the liquid. Most air-lift pumps do not realize this ideal objective, but are more prone to a degree of slug-flow. However, too much increase in the gas volume over and above the inert gas bubbles originally injected into the upleg of a gas-lift device operating on liquid scrap containing large amounts of dissolved carbon and oxygen could result in the liquid phase becoming the dispersed phase in a much greater volume of continuous gas phase. Complete inversion of this type would make a gas-lift pumping system inoperative and the desired goal of pumping the liquid scrap to the top of the reduced pressure desorption tower would not be accomplished.

On the basis of the various considerations just discussed, there is a perceived need to provide completely backmixed reservoir vessels or liquid sumps, which are provided with product inflow and overflow or withdrawal, located throughout the flow circuit under discussion, whenever liquid scrap is to be transferred from a low pressure region to the next in-line processing stage. The 20 t/min figure which has been demonstrated in commercial practice to overcome the difficulties associated with rapid evolution of carbon monoxide for the Fuji conditions of upleg and downleg snorkels of given sizes, can be identified with the maximum pressure of carbon monoxide that can be developed in the system and which can be evaluated mathematically by the expression for the equilibrium pressure of carbon monoxide developed above molten steel containing specified levels dissolved carbon and oxygen (E. T. Turkdogan, "Fundamentals of Steelmaking," The Institute of Materials, London, (1996). For the present case, the product of percentage carbon times ppm oxygen all divided by 20 is equal to or less than  $(0.055)(500)/20 = 1.375$ . This figure is the equilibrium pressure in atmospheres of carbon monoxide that could be generated. If an attempt were made to remove such a melt from an RH vessel through a barometric seal or downleg nozzle with an internal diameter of 150mm, comparable to that in the Fuji plant, at a rate equivalent to a product flow of say 0.5 Mtpa i.e.

0.95 t/min as opposed to 20 t/min, it would be rendered totally inoperative. No melt would be discharged out rather it would accumulate within the vacuum vessel.

Provision of a multiplicity of back-mixed liquid sumps to accommodate large recirculation rates between the various processing stages, with superimposed product flowrate entry and discharge as implied above, is a viable approach, which in certain circumstances may be the only realistic option available, because of process constraints overriding other considerations. For example, it may be that the process chemistry demands high levels of dissolved carbon on thermodynamic grounds, while interfacial chemical kinetics are favoured by having at least a certain minimum dissolved oxygen concentration. However, in many cases a far simpler option may be available, in which case the preferred embodiment may turn out to be along the lines now to be developed.

In response to the foregoing discussion it seems reasonable to propose that one preferred embodiment must focus on decreasing the propensity for CO generation, which essentially means establishing either or both low levels of dissolved carbon or oxygen before any reduced pressure continuous refining for removal of copper and tin on steel stream flow rates typical of actual steel production rates. Even so it would seem prudent in the first instance not to attempt these procedures for relatively small-scale processing, but rather attention should be focused on continuous processing of liquid scrap at rates of say 0.5 Mtpa or greater, so that at least some carbon monoxide evolution can be tolerated without such evolution totally disrupting the continuity of liquid scrap flowing through the various sub-systems involved. If lesser throughputs of liquid scrap are to be continuously treated for removal of copper and tin under reduced pressure, a preferred embodiment would incorporate decarburization to a very low level using either an ultra low carbon (ULC) refining step or alternatively deoxidation by an addition of metallic or alloy reagents via the RH melt circulation system.

Decarburization of liquid scrap occurs spontaneously during scrap melting based on melt circulation. Some carbon is introduced into the system over and above the carbon content of the steel itself, because of extraneous carbonaceous contamination derived from pyrolysis of oil, grease, plastics, vegetable matter and residual foodstuffs originally in the charge material on the inert gas side of the melt circulation loop. Natural gas or other combustible gas firing on the other arm of the melting loop to provide the energy requirements for melting, automatically establishes open channel decarburization in which dissolved carbon is oxidized in preference to iron at a rate controlled principally by liquid phase mass transfer of solute carbon to the free surface from the bulk of the liquid scrap, once a relatively low steady state carbon level is established throughout the scrap melting loop. Melt circulation based on RH degasser technology contributes to further continuous decarburization with the proportion of the total decarburization due to the RH-type unit capable of being varied at will by controlling the degree of vacuum applied.

Depending on the origin of the steel scrap, especially prior incineration, and extent of air infiltration because of negative draft requirements on health and safety grounds, the oxygen content of the liquid scrap should in most cases should be relatively low, provided there is enough solute carbon in the liquid scrap to sustain liquid phase mass transfer to the liquid/gas interface to satisfy the diffusional supply of oxidant by gas phase mass transfer to the free melt surface on the heat input arm of the melting loop. The fundamental mechanisms involved here and their quantitative manipulation in order to establish an acceptable steady state, have been discussed in a related paper

(N.A. Warner: *Ironmaking & Steelmaking*, 2003, vol. 30 (6), 429-434). In this connection, it is worth noting that the provision of a recirculated argon/inert gas based scrap preheating system, which itself is deoxidized to a very high level by intimate contacting with molten aluminium, ensures negligible oxidation of charge materials both while being preheated to around 900°C and then assimilation into the argon-blanketed arm of the melting loop without direct contact with the combustion gases at any stage. These are positive beneficial attributes in terms of steel cleanliness and ultimate consumption of deoxidiser.

To gain further insight into the potentially disruptive effects of uncontrolled carbon monoxide evolution in continuous steelmaking involving reduced pressure gas/liquid contacting, it is worth noting the very large gas volumes which could be generated relative to the volume of the liquid steel itself. For example, 1 m<sup>3</sup> of steel containing a mere 2ppm of dissolved oxygen would produce about 69 m<sup>3</sup> of gas at 2 mbar total pressure and 1600°C, if it were fully degassed by carbon/oxygen interaction. However, in this case the equilibrium pressure of carbon monoxide is relatively small and bubbles are unlikely to form beneath the surface of the melt and, of course, kinetic factors would in any case limit the amount of carbon monoxide actually evolved at the free melt surface.

The relationship between the pressure of carbon monoxide  $p_{CO}$ , the pressure in the vessel  $P_o$ , the depth  $h$  beneath the free liquid surface, the radius  $r$  of the bubble, density of the melt  $\rho$  and surface tension  $\sigma$  of the melt is given by

$$p_{CO} = P_o + \rho gh + 2\sigma/r \quad [6]$$

In this expression,  $\rho gh$  is equivalent to the hydrostatic pressure, sometimes called the ferrostatic pressure, and  $2\sigma/r$  is the excess pressure across the bubble surface. If  $p_{CO}$  is greater than the carbon monoxide equilibrium pressure, a bubble could not form irrespective of issues relating to homogenous or heterogeneous nucleation. Thus for a ULC melt with say 20 ppm carbon, it can be shown that with 300 ppm dissolved oxygen, a bubble could not form any deeper than 3 cm from the free melt surface. Accordingly, continuous removal of steel from the bottom of a reduced pressure desorption tower, for example, via a barometric leg could proceed without complication simply by providing a minimum depth of melt of at least 3 cm in the base of the tower directly above the entrance to the barometric leg. For bubble formation to occur within the liquid pool at the base of the tower, which is virtually impossible on homogeneous nucleation grounds, the mechanism would have to involve gas bubble detachment from porosity in the refractory base. Similarly, in the top region or upper level sump, for example, for liquid scrap receiving radiation from an array of electrically heated graphite rods positioned above the entering melt surface on its way to the reduced pressure desorber, bubble formation and the associated liquid splashing, must be avoided to prevent attack on the rods as well as carbon pickup into the steel melt. Accordingly, the same considerations apply here as to those already discussed in relation to the barometric leg.